

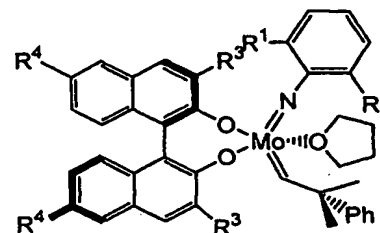
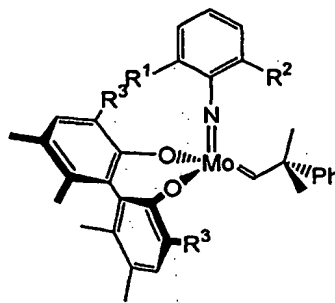
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(54) Title: ASYMMETRIC METATHESIS REACTIONS INVOLVING ACHIRAL AND MESO SUBSTRATES

(57) Abstract

A composition and method for the catalytic conversion of a racemic mixture of dienes to a cyclic olefin by a ring-closing metathesis (RCM) reaction are disclosed. The composition, a transition metal complex with an M=C reaction site, contains a bidentate dialkoxide of at least 80 % optical purity. Because the M=C reaction site is of a sufficient shape specificity, conferred in part by the dialkoxide of sufficient rigidity and a M=N-R¹ site, reacting the composition with a mixture of two enantiomeric dienes results in an olefin metathesis product that has at least a 50 % enantiomeric excess of one enantiomer in the mixture. A method is also provided for reacting a composition with a racemic diene mixture to generate a metathesis product that has an enantiomeric excess of at least 50 %. Methods are also provided for catalytic enantioselective desymmetrization. One method involves an olefin metathesis reaction with a molecular substrate having a plane of symmetry to form a product free of a plane of symmetry. Another method provides a desymmetrization reaction to occur in the absence of solvent. A method for producing quaternary carbon centers through a desymmetrization reaction is also described.



- 1a: R³ = *t*-Bu; R¹ = R² = *i*-Pr
 1b: R³ = *t*-Bu; R¹ = R² = Me
 1c: R³ = adamantyl; R¹ = R² = *i*-Pr
 1d: R³ = adamantyl; R¹ = R² = Me
 1e: R³ = ethyl; R¹ = R² = *i*-Pr
 1f: R³ = ethyl; R¹ = R² = Me

- 2a: R³ = 2,4,6-tri(*i*-propyl)phenyl;
R¹ = R² = *i*-Pr;
 2b: R³ = 2,4,6-tri(*i*-propyl)phenyl;
R¹ = R² = Me
 2c: R³ = *t*-Bu; R¹ = R² = *i*-Pr;
R⁴ = *t*-Bu
 2d: R³ = *t*-Bu; R¹ = R² = Me;
R⁴ = *t*-Bu
 2e: R³ = Ph; R¹ = R² = *i*-Pr, R⁴ = H
 2f: R³ = Ph; R¹ = R² = Me, R⁴ = H

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